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Full Length Article

Pore structure of transitional shales in the Ordos Basin, NW China: Effects of composition on gas storage capacity

Fengyang Xiong [a,b], Zhenxue Jiang [a], Peng Li [c], Xiangzeng Wang [d], He Bi [e], Yirun Li [a], Ziyuan Wang [f], Mohammad Amin Amooie [b], Mohamad Reza Soltanian [b], Joachim Moortgat [b,*]

[a] *State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing 102249, China*
[b] *School of Earth Sciences, The Ohio State University, Columbus, OH 43210, USA*
[c] *Petroleum Exploration and Production Research Institute, SINOPEC, Beijing 100083, China*
[d] *Shaanxi Yanchang Petroleum (Group) Corp. Ltd., Xi'an 710075, China*
[e] *Research Institute of Petroleum Exploration & Development, PetroChina, Beijing 100083, China*
[f] *School of Earth and Space Science, Peking University, Beijing 100080, China*

HIGHLIGHTS

- Pore structure of transitional shale and organic matter is measured by N_2, CO_2 isotherms.
- Both organic and inorganic grains develop micro-, meso- and macropores in gas window.
- Clay minerals control specific surface area and absorbed gas at over-mature stage.
- High TOC increases *micropore* volume at high depth, while *total* pore volume decreases.

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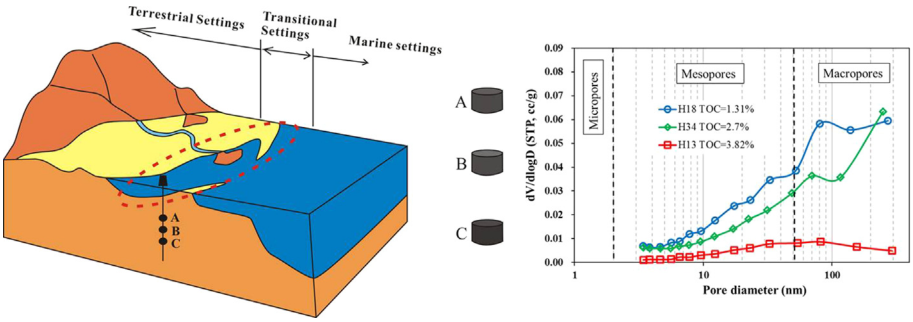
GRAPHICAL ABSTRACT



ABSTRACT

The recoverable resource of shale gas is 25 trillion cubic meter, 33% of which is stored in *transitional* shales in China. This work investigates the effects of organic and inorganic compositions on the development of Upper Paleozoic *transitional* shale pore structures through a combination of petrophysical and geochemical measurements. 42 shale samples were collected from marsh-lagoon and coastal delta settings in the Ordos Basin, NW China. The samples include the Upper Permian Shanxi shale (average total organic carbon (TOC) of 1.58 wt%, Type III kerogen, average vitrinite reflectance (Ro) 2.6%), and the Upper Carboniferous Benxi shale (average TOC of 1.91 wt%, Type III kerogen, average Ro 2.74%) at the over-mature stage or dry gas window. An important characteristic of these shales is the large proportion of clay minerals (~69% in Benxi shale and 54% in Shanxi shale). The quartz content is ~17% and 40% for Benxi and Shanxi shales, respectively. The pore structure of three samples and one isolated kerogen sample is analyzed via both low-pressure nitrogen and carbon dioxide adsorption methods. Low pressure nitrogen adsorption experiments show that Benxi and Shanxi shales characterized by ultra-low porosity and permeability develop mainly silt-shaped pores and potentially ink-bottle-shaped pores. We find that increasing fractions of organic matter (OM) result in a decrease in both total pore volume and specific surface area (SSA). Low pressure carbon dioxide adsorption experiments show that micropore volumes nonlinearly increase with increasing OM, although the contribution of organic micropore volume is limited. The mesopore and macropore volumes of inorganic compositions contribute mostly to the total pore

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* Corresponding author.
E-mail address: moortgat.1@osu.edu (J. Moortgat).

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volume. The OM in transitional shales in Yanchang mainly develop *mesopores* (with <5 nm diameters), which significantly contribute to the SSA, while *micropores* are the main contributor to SSA in the inorganic matter. For thermally over-mature transitional shales, clay minerals contribute the most to SSA and pore volume as well as the storage capacity of absorbed and free gas.

1. Introduction

During the past two decades, the shale gas revolution has dramatically changed the natural gas market structure in the US and China. This is related to the success of emerging technologies in horizontal drilling and hydraulic fracturing [1–8]. Approximately one third of the US energy consumption is from natural gas compared to other fossil fuels and renewable energies [9]. Shale gas is recognized as the cleanest fossil fuel [10]. In 2015 it produced ~47% of US natural gas, up from 34% of the total U.S. dry natural gas production in 2011 [9].

Increasing commercial importance has drawn more attention to shale and shale gas [11–16]. Understanding the pore structure of shales is critical in the evaluation, exploration and exploitation of shale gas. The pore system of gas shales are commonly characterized by, micropores (pore diameter <2 nm), mesopores (2–50 nm) and macropores (>50 nm) [17]. Shale gas has been recognized to exist in three phases: 1) compressed free gas in the shale pore space, 2) adsorbed gas on the surface of organic pores and clay minerals and 3) dissolved gas in the fluid and organic matter within shales [18]. Free gas is frequently calculated by the reservoir pore volume and gas equation-of-state, which is a function of pressure, temperature, and gas compressibility factor. The amount of free gas is thought to correlate well to the volume of meso- and macropores, which account for most of the absolute pore volume. Adsorbed gas has a much higher (heterogeneous) density than free gas at the same temperature and pressure and accounts for most of the gas in micro- and mesopores. Adsorption may account for 20%–85% of total shale gas-in-place (GIP) [18,19]. Its contribution is commonly estimated by high pressure methane adsorption isotherms. Recent studies show that dissolved gas could also be significant in oil-window mature shales. The fraction of dissolved gas correlates with organic pores, fluid and reservoir pressure, and temperature [20,21].

Unlike conventional resources, shale has long been thought of as a source rock, characterized by ultra-low porosity and permeability matrix and extreme heterogeneity. Loucks et al. [12] suggested that organic matter (OM) within shales controls the development of abundant nanopores and plays a significant role in shale gas storage [20–29].

OM in marine and continental gas shales has been shown to principally contribute to the development of micropores and mesopores as well as clay minerals. These are the main contributors to *adsorbed* gas. Inorganic particles mainly develop macropores that provide the *free* gas storage [20,22,25–31]. The development of organic pores is complicated by the content, type, and maturity of OM [12,28,32–34]. Kerogen is often classified into three types: I, II, and III. Higher kerogen types (e.g., III) typically have larger fractions of micropores, gas-wet aromatics, and polar function groups [22,28], which together provide a higher adsorption capacity.

The total organic carbon (TOC) content is positively correlated with shale gas adsorption capacity and content of shale gas [22,28,35–38]. However, exceptions do exist because the contribution of clay minerals can complicate shale gas adsorption capacity and content. It has recently been suggested that OM can develop nanopores in pyrobitumen and kerogen and that organic porosity generally increases with increasing maturity [39–45].

However, many researches have mainly focused on marine and terrestrial shales and less attention has been given to transitional shales [4,21,41–43,46–51]. Transitional shale refers to the shale deposited between terrestrial and marine settings, e.g., lagoon, delta, beach and tidal flat. In addition, the role of OM in transitional shales remains poorly understood. Low pressure carbon dioxide and nitrogen isotherms are universally used to characterize pore size distribution of micropores and mesopores, respectively [20,23,31]. Previous studies mainly focused on the relationship between TOC and shale gas adsorption capacity and content [24,28,31,52]. However, few studies were conducted on the pore structure of isolated kerogen.

The Late Paleozoic transitional shales in Ordos Basin distribute widely and develop dark organic rich shales. It is regarded as one of the most important transitional shale gas targets in China [53]. The goal of this paper is to investigate the pore structure of transitional shales in Ordos Basin. We focus on the effect of shale composition on the formation of pore size distribution. We present geochemical and petrological characteristics of transitional shales in Section 3.1 and 3.2. The roles of OM in transitional shale pore system as well as shale gas storage are considered in Section 3.3.

2. Samples and experiments

2.1. Geological setting and samples

The Ordos Basin is the second largest sedimentary basin in China. It is a craton basin located on the central North China Plate that consists of six 2nd order structural units. Our study area is part of the Yanchang Oilfield on the southern Yishan slope (Fig. 1).

The transitional shale samples are from recently drilled wells (Q14 and Q25) that target the Upper Carboniferous Benxi and the Lower Permian Shanxi (Fig. 2) with an average thickness of 30 and 95 m in the study area, respectively. These shales were deposited in marsh-lagoon and coastal delta environments, and developed sandstone, coal, and dark shale/mudstone that widely distributed in the tectonically stable Ordos Basin.

During the past few years, Yanchang Oilfield Company has targeted the Upper Triassic mature lacustrine Chang 7 and 9 shales as potential terrestrial shales for shale gas and oil with vitrinite reflectance of 0.83%–1.10%. Recently, Benxi and Shanxi shales, which are buried by over 3000 m, were targeted to investigate the shale gas capacity of transitional shales due to the kerogen of type III and higher thermal maturity than Triassic lacustrine shales. There were 42 core samples collected from Q14 and Q25 wells to carry out geochemical experiments. 38 of the 42 samples were further used for petrological measurements. Three of the 38 samples with different TOCs were further chosen to characterize the pore structure of the Late Paleozoic transitional shales and the effects of shale composition on pore size distribution of transitional shales.